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(21) International Application Number: PCT/FI90/00027 (22) International Filing Date: 24 January 1990 (24.01.90) (30) Priority data: 890427 27 January 1989 (27.01.89) FI (71) Applicant: NESTE OY [FI/FI]; Keilaniemi, SF-02150 Espoo (FI). (72) Inventors: ÖSTERHOLM, Jan-Erik ; Kurjentie 5 E, SF-06100 Porvoo (FI). LAAKSO, Jukka ; Ruusulankatu 16 B 24, SF-00250 Helsinki (FI). NYHOLM, Per ; Viikintie 11 A 14, SF-06150 Porvoo (FI). TAKA, Tapani ; Humaltarhantie 3 D 19, SF-06450 Porvoo (FI). KARJALAINEN, Sari ; Suolakatie 3 A 459, SF-06400 Porvoo (FI). MONONEN, Pirjo ; Suolakatie 1 A 26, SF-06400 Porvoo (FI).		(74) Common Representative: NESTE OY; Corporate R&D, Patent Services, P.O.B. 310, SF-06101 Porvoo (FI). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: USE OF ELECTRICALLY CONDUCTING POLYMER COMPOSITES (57) Abstract <p>The subject invention is direct towards novel use of a polymer composite as thermoplastic raw material for products with electrically conducting or semiconducting properties. In polymer composites known in the field electrically conducting fillers and polymers do not have thermoplastic properties and are accordingly ill suited for thermoplastic processing of conducting and semiconducting products. It has now been invented that a polymer composite made up of an electrically nonconducting polymer matrix or polymer substrate, doped or undoped poly(3-substituted thiophene) and possibly plastics additives, is well suited as raw material for thermoplastics with conducting or semiconducting properties. The invention is accordingly also directed towards antistatic and semiconducting applications, where good shielding against electromagnetic interference is required and applications where the discovered piezoelectric properties of this material can be used.</p>		

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Use of electrically conducting polymer composites

The invention relates to the use of such electrically conducting polymer composites, which are made of a polymer matrix or a polymer substrate, intrinsically conducting, doped or undoped poly(3-substituted thiophene) and possibly additives for plastics.

Electrically conducting polymer materials can be roughly divided into two different categories: filled electrically conducting polymer materials and intrinsically electrically conducting polymer materials.

The former are composites, which consist of an electrically nonconductive polymer matrix or substrate and into which has been mixed or onto which has been layered an electrically conducting material. Usually these composites have as electrically conducting material carbon black, carbon fibers, metal flakes or metal fibers, which have been mixed into the matrix material in the melt state or layered onto the surface of a polymer substrate. In this kind of composites the electrical conductivity depends on the contact between the filler particles. Usually 10 - 50 weight-% well dispersed filler is needed to achieve composites with high conductivity. There are, however, many problems with composites of this kind. The mechanical properties of the composites decrease as the portion of filler is increased, the electrical conductivity is difficult to control especially in the semiconducting region 10^{-9} - 10^{-3} S/cm and homogenous dispersion of the filler in the matrix is difficult.

Intrinsically electrically conducting polymers are substances, which as such are insulators, but can be made conducting by adding to them certain doping or agents. They are polymers with long conjugated chains with double bonds.

The pi electronic system of the double chains can be perturbed by adding the mentioned doping agents, which are either electron donors or acceptors. Through this process holes or excess electrons are created in the polymer chain which make the propagation of electricity possible.

The electrical conductivity of intrinsically conducting polymers can be controlled depending on the dopant concentration so that it spans almost the whole conductivity scale from insulators to metals. Examples of polymers of this kind are poly(acetylene), poly(p-phenylene), poly(pyrrole), poly(aniline) and poly(thiophene).

Also known in the field are plastic composites which are made of in addition to a non-conducting polymer matrix or substrate of an intrinsically conducting polymer as mentioned above. Galvin and Wnek have in their publication in Polym. Commun., 23, (1982), 795, proposed the polymerization of poly(acetylene) into a polyethene film impregnated with catalyst. Lindsay and Street have in Synthetic Metals, 10:67, 1985, proposed the electrochemical polymerization of polypyrrole into a plastic matrix to make a conducting composite, whose mechanical properties are better than those of pure polypyrrole. In the publication Björklund R.B. and Lundström I., Electronic Materials, Vol. 13, no. 1, 1984, 211-230 and the DE patent application 3 321 281 pyrrole has been used as the electrically conducting component of polypyrrole-cellulose composites. The US patent publication 4 604 427 presents the diffusion of pyrrole or aniline monomer into a matrix polymer, after which the impregnated matrix polymer is treated with FeCl₃ in order to make an electrically conducting composite, where the conductor is polypyrrole or polyaniline.

A plastic composite consisting of an intrinsically electrically conducting polymer and a non-conducting polymer matrix

should be expected to have properties than a plastic composite with carbon or metal fillers. The electrically conducting polymers mentioned are, however, insoluble and non-processable, i.e. thermoset, which prevents their melt processing and in this way hinders their use in different applications.

The purpose of the invention at hand is to achieve such use of an electrically non-conducting polymer matrix or substrate and an intrinsically electrically conducting polymer, where it works as raw material for partly or wholly conducting thermoplastic products. The aim is also to achieve thermoplastic conducting or semiconducting products that have practical processing properties in the melt, rubberlike and liquid suspended state. This has been achieved with use according to claim 1 and with conducting and semiconducting products as described in claim 6.

The use of a composite made of a non-conducting polymer matrix or substrate and an intrinsically electrically conducting polymer as thermoplastic material has now been achieved by choosing poly(3-substituted thiophene) as the conducting polymer. In accordance with the subject invention a thermoplastic conducting or semiconducting product has accordingly been achieved with the kind of polymer composite mentioned containing poly(3-substituted thiophene). With a thermoplastic material and product is meant in this case a material or product processed in the melt, rubberlike or liquid suspended state. In the liquid suspended state the processing is done e.g. by paste moulding, where paste consisting of e.g. PVC and poly(3-substituted thiophene) is moulded and hardened by heating. Poly(3-substituted thiophene) can also be added to latex intended for coating purposes.

Processing in the rubberlike state can be done e.g. by vacuum moulding, pressure moulding or heat forging.

The most advantageous is the use of such a polymer composite, where the conducting or semiconducting product is made by melt processing. Advantageous melt moulding and casting methods are extrusion by which e.g. profiles, sheets, blow moulded films and products are made, injection moulding by which formed pieces and blow moulded products are made, rotational moulding by which hollow small products are made, and melt calendering in which plastic coating films are made between heated cylinders. Among less common melt processing methods are compression moulding and transfer moulding.

The electrically conducting polymer used in the invention poly(3-substituted thiophene) is exceptional compared to other conducting polymers in the respect that it has the properties of a thermoplastic. It can be solved in organic solvents as toluene, chloroform and tetrahydrofuran and it melts without decomposing between 170 and 195 °C, at which temperature it is melt processable and possible to mix into e.g. a matrix plastic. In the invention at hand it is advantageous to use poly(3-alkyl thiophene) and most advantageous to use poly(3-octyl thiophene). The latter polymer is produced by polymerizing 2,5-diiodide-3-octyl thiophene.

The electrically non-conducting plastic component can be any thermoplastic, which is melt processable and compatible with poly(3-substituted thiophene). Advantageous matrix or substrate plastics are homo- or copolymers of ethene or some other olefin, vinyl chloride or styrene. As a suitable polymer ethene vinyl acetate copolymer can be mentioned.

The additives used in the polymer composite depend on the plastic component of the composite and they can in addition

to other polymers be fillers, plasticisers, lubricants, stabilizers, antioxidants, antistatic agents, fire retardants, pigments, UV absorbants, expanders for cellular plastics or cross linking agents.

The mixing together of the electrically conducting polymer component and the non-conducting polymer component can be done with any known device in the field, e.g. with a Brabender mixer or screw extruder. The mixing is done in the temperature range 150 - 200 °C, advantageously in the range 160 - 185 °C. Approximately 0.1 - 50 weight-% of poly(3-substituted thiophene) is added to the melt mixture and accordingly 50 - 99.9 weight-% other polymer and/or additives. An advantageous amount of the electrically conducting polymer is 5 - 30 weight-%.

The production of a electrically conducting polymer composite has been described above, but the composite can also be made by pressing a layer of poly(3-substituted thiophene) in melt, rubberlike or liquid suspended state on the surface of a non-conducting polymer substrate.

The doping of the polymer composite can be done before the thermoplastic moulding of the electrically conducting poly(3-substituted thiophene) with the matrix or substrate polymer, or advantageously so that the moulded thermoplastic composite is doped after processing.

Doping is achieved either chemically or electrochemically with electron donating or accepting agents. It is advantageous to treat the polymer composite with a medium containing FeCl_3 . The medium can be a suitable organic solvent, e.g. nitro methane or any other solvent or suspension medium, that does not have a negative effect on the doping event for instance by solving the poly(3-substituted thiophene). Usually such solvents which solve doping agent (e.g.

salt) in question and swell the composite to enable the doping event to take place. Another favourable doping agent is iodine which is used as such to increase the conductivity of the poly(3-substituted thiophene). The different doping treatments can also be applied simultaneously.

After doping the product is washed clean of doping agent with a suitable solvent, most favourably with the same solvent used in the doping of the material, and finally the composite is dried.

Depending on the application in question the conductivity of the composites in question can be controlled by varying the doping time, the dopant concentration or the amount of poly(3-substituted thiophene) in the composite. In this way the whole conductivity range, including low conductivities, can be covered. In addition only the amount needed of the poly(3-substituted thiophene) is only approximately a third of the amount of carbon black needed to achieve sufficient conductivity in composites containing carbon black. Accordingly the mechanical properties of the composites are hardly affected at all.

The conducting and semiconducting products in the invention in which poly(3-substituted thiophene) is used contain a polymer composite have depending on the doping conditions a conductivity in the range 10^{-9} - 10 S/cm. Their shielding efficiency against electromagnetic interference (EMI) is also considerable. Their EMI shielding efficiency is clearly better than a surface painted with carbon paint.

Products in which poly(3-substituted thiophenes) subject to the invention are e.g. antistatic applications as floorings, interior coatings, different packing materials, conveyor belts, storage and transport containers for explosives and flammable substances and charging tubes for explosives. The

composite can also be used for electromagnetic shielding and it is applicable in power cables as a semiconducting shielding layer. It can be made into electronic products such as sensors, circuit boards, switches, heating elements, monitors and components. The polymer composite is also suited for battery applications, optical and photovoltaic applications, and paraboloid antennae and radar reflectors.

The products subject to the invention are also electrical and are accordingly suited for electrical applications.

In the following some products and applications of the subject invention are presented.

Fig. 1 shows the dependency of the electrical conductivity as a function of time in a composite as presented in example 1.

Fig. 2 shows the shows the EMI shielding efficiency for different products as presented in example 3, where the polymer matrix is EVA.

Fig. 3 shows the shows the EMI shielding efficiency for different products as presented in example 3, where the polymer matrix is PVC.

Fig. 2 shows the shows the EMI shielding efficiency for different products, where the polymer matrix is 80 weight-% EVA, PVC and polystyrene.

Fig. 2 shows the shows the EMI shielding efficiency for different products as presented in example 3, where the polymer matrix is polystyrene.

Example 1

A polymer composite was made by melt processing at 170 - 195 °C made of 10 % poly-3-octyl thiophene and 90 % ethylene vinyl acetate polymer. The melt processing was carried out in a Brabender mixer for 10 minutes and mixing speed 30 r/min. The obtained composite was doped for different lengths of time by submerging it in a FeCl₃-nitro methane solution in dry Argon atmosphere. The conductivity of the composite varied depending on doping time between 10⁻¹⁰ and 10⁻¹ S/cm as shown in fig.1. A polymer composite with a conductivity in this range is well suited for antistatic and semiconducting applications. After a doping time of 1 hour the conductivity was 0.6 S/cm.

Example 2

Poly(3-octyl thiophene) was pressed in the melt state on the surface of a ethylene vinyl acetate substrate. The pressing time was 5 minutes, the temperature 180 °C and the pressure 100 bar. The in this way obtained polymer composite was doped with iodine in vacuum and in addition with FeCl₃ in nitro methane. The achieved conductivity of the composite was 10 S/cm.

Example 3

A polymer composite was made by melt processing at 170 - 195 °C made up of different amounts of poly(3-octyl thiophene) and ethylene vinyl acetate (EVA), vinyl chloride (PVC) or styrene polymer. The composite was doped by submerging into FeCl₃-nitro methane solution.

The electromagnetic shielding efficiency of the composite was measured in the range 100 kHz - 1 GHz. By adjusting the mixture ratio of the composite described in examples 1 and 2 and the doping composites suitable for different applications were achieved. The shielding efficiency was measured according to standard ASTM ES-7/83 for different composites

and e.g. a composite with 20 weight-% poly(3-octyl thiophene) and 80% EVA and doped with FeCl_3 , the shielding efficiency in the near field was above 50 dB up to 1 MHz frequency. The shielding efficiency of a PVC-poly(3-octyl thiophene) is above 40 dB up to a frequency as high as 50 MHz. At higher frequency the shielding efficiency of all the measured composites with 20 weight-% poly(3-octyl thiophene) decreases to 10 dB at 1 GHz frequency. The shielding efficiency of poly(3-octyl thiophene) composites is noticeably higher than that of a surface treated with carbon paint (cf. fig. 2 - 5)

Due to the fact that the shielding efficiency of the material is dependent on the ability of the material to reflect electromagnetic radiation (e.g. radio waves) the material described in examples 1, 2 and 3 can also be used in paraboloid antennae e.g. in the manufacture of satellite antennae.

Example 4

An electrical heating test was performed on a sheet made of undoped and doped poly(3-octyl thiophene) The temperature of the polymer increased to 50 °C due to the current with a voltage of 5 V. The polymer can accordingly be used as a heating element and as a sensor.

Example 5

A test for piezoelectrical activity was performed on a 0.2 mm thick poly(3-octyl thiophene) film. Pressure changes affected on the polymer induced an electric voltage across the samples. The polymer can accordingly also be used in piezoelectrical applications, e.g. pressure sensor.

Patent claims

1. The use of such a polymer composite that is made of a polymer matrix or polymer substrate, intrinsically electrically conducting poly(3-substituted thiophene) and possibly plastics additives as raw material for products with conducting or semiconducting properties.
2. Use according to patent claim 1, where the products with conducting or semiconducting properties are made by melt processing, e.g. extrusion, injection moulding, melt spinning, rotational moulding, calendering, compression moulding or transfer moulding.
3. Use according to patent claim 1 where the products with conducting or semiconducting properties have been made by moulding in rubberlike state, e.g. vacuum moulding, pressure moulding or heat forging, or in suspension, e.g. by paste moulding or using latex technique.
4. Any use in the claims above where the poly(3-substituted thiophene) advantageously is poly(3-octylthiophene).
5. Any use in the above claims where the polymer matrix or substrate is the polymer of ethylene or some other olefin, vinyl chloride or styren, or their copolymer, advantageously ethylene vinyl acetate copolymer.
6. A product with conducting or semiconducting properties, where its raw material is a composite made of polymer matrix or substrate, an electrically conducting solid and possibly other additives, known for having as its electrically conducting solid intrinsically conducting, doped or undoped poly(3-substituted thiophene).

7. A product according to claim 6, known to be an antistatic product, e.g. flooring, interior coating, package, conveyor belt or storage or transport container or transport tube for flammable or explosive substances.

8. A product according to claim 6, known to be a sensor, circuit board, switching device, heat element, monitor or electronic component or protective or shielding layer for electric cables.

9. A product according to claim 6, known to be a part of a battery.

10. A product according to claim 6, known to be a part of a paraboloid antenna or radar reflector.

11. A product according to claim 6, known to be a piezo electric element.

12. A product according to claim 6, known to be a photo-optical or photoelectrical element.

INTERNATIONAL SEARCH REPORT

International Application No **PCT/FI 90/00027**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: H 01 B 1/12, C 08 L 65/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ?		
Classification System	Classification Symbols	
IPC5 H 01 B		
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ** with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A1, 0203438 (ALLIED CORPORATION) 3 December 1986, see column 3, line 1 - line 7; column 4, line 1 - line 7; column 5, line 42; column 11, line 39 - line 56 column 14, line 38 - column 15, line 4 --	1,4-6,8- 12
X	EP, A2, 0246931 (SUMITOMO CHEMICAL COMPANY, LIMITED) 25 November 1987, see page 2, line 44 - line 60; page 5, line 33 - line 37 --	1,6
X	EP, A1, 0257573 (HOECHST AKTIENGESELLSCHAFT) 2 March 1988, see page 2, line 17 - line 40; page 8, line 28 - line 35 --	1,6- 12
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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X	WO, A1, 85/05728 (BATTELLE-INSTITUT E.V.) 19 December 1985, see page 3, line 7 - line 24; page 9, line 21 - line 31 ---	1-3,5- 12
A	EP, A1, 0240063 (SOLVAY & CIE (SOCIÉTÉ ANONYME)) 7 October 1987, see page 2, line 37 - line 39; page 3, line 54 - line 58 ---	1,4,6,9
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/FI 90/00027**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.

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